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# Theoretical characterization of the low-lying excited states of the CuCl molecule

C. Sousa, W. A. de Jong, R. Broer, and W. C. Nieuwpoort

Department of Chemical Physics and Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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The character of the low-lying excited states of diatomic CuCl is studied primarily by means of the complete active space self-consistent field (CASSCF), method and a second order perturbation approach with the CASSCF wave function as reference state [complete active space perturbation theory to second order (CASPT2)]. For comparison, the lower levels of the spectra of the  $\text{Cu}^+$  ion are also analyzed. A first order treatment of the scalar relativistic effects, the mass-velocity and Darwin terms, is included in the calculations. The importance of spin-orbit interactions is investigated by comparing our nonrelativistic valence shell CI (VCI) and relativistic results obtained with our four-component program suite MOLDIR. The six lowest excited states of the CuCl molecule, which are related to the  $\text{Cu}^+(3d^9 4s^1)\text{Cl}^-(3s^2 3p^6)$  ionic configuration, are assigned. The assignments agree with earlier theoretical work. Where they can be compared, the calculated spectroscopic constants are in good agreement with the experimental data. © 1997 American Institute of Physics. [S0021-9606(97)03017-1]

## I. INTRODUCTION

Copper halides exhibit rather confusing optical spectra, the heavier the halide the more complicated the spectrum. Only for the lightest halide, CuF, the nature of the low-lying excited states has been well established both theoretically<sup>1-6</sup> and experimentally.<sup>7-9</sup> For CuCl the situation is less clear. Although it is generally agreed that all excitations reported have a common lower state, the ground state  $X^1\Sigma^+$ ,  $\text{Cu}^+(3d^{10})\text{Cl}^-(3s^2 3p^6)$  and that the excited states involved in such transitions arise from the  $\text{Cu}^+(3d^9 4s^1)\text{Cl}^-(3s^2 3p^6)$  ionic configuration, the assignment of the observed bands to particular states is still not well established.

The visible spectrum of CuCl was first reported by Ritsch<sup>10</sup> and Bloomenthal<sup>11</sup> who observed five bands, all of them having a common lower state. Many years later, Rao *et al.*<sup>12-14</sup> reported the existence of new bands. Six emission band systems were characterized;  $A(19\,035\text{ cm}^{-1})$ ,  $B(20\,486\text{ cm}^{-1})$ ,  $C(20\,648\text{ cm}^{-1})$ ,  $D(22\,987\text{ cm}^{-1})$ ,  $E(23\,067\text{ cm}^{-1})$ , and  $F(25\,326\text{ cm}^{-1})$ . Rotational analysis was carried out by Lagerqvist *et al.*<sup>15</sup> who assigned the  $B$  and  $C$  systems to the  $^1\Pi \rightarrow X^1\Sigma^+$  and  $^1\Sigma^+ \rightarrow X^1\Sigma^+$  transitions, respectively. Rao *et al.*<sup>12-14</sup> and Ahmed *et al.*<sup>16</sup> assigned the  $A$ ,  $D$ , and  $F$  systems to excitations from the  $X^1\Sigma^+$  to the  $^1\Pi$  state and the  $E$  band to the  $^1\Sigma_1^+ \rightarrow X^1\Sigma^+$  transition. Burghardt *et al.*<sup>17</sup> investigated the  $D$  and  $E$  states by laser excitation spectroscopy. The  $E$  state was assigned to a  $^1\Sigma^+ \rightarrow X^1\Sigma^+$  transition while the  $D$  state was suggested to be a  $^1\Pi \rightarrow X^1\Sigma^+$  rather than a  $^3\Delta_1 \rightarrow X^1\Sigma^+$  transition. However, according to these authors, this state is unlikely to be pure but rather a mixing of the two  $^1\Pi_1$  and  $^3\Delta_1$  states. Balfour *et al.*<sup>18</sup> measured a new band in the red region at  $13\,507.9\text{ cm}^{-1}$ , called the  $A'$  system, and assigned it to a  $^3\Sigma_1^+ \rightarrow X^1\Sigma^+$  transition. A similar  $A'$  band was already observed in the CuF molecular spectra<sup>7</sup> and recently also in the

CuBr spectra.<sup>19</sup> In both cases the band was ascribed to a  $^3\Sigma_1^+ \rightarrow X^1\Sigma^+$  electronic transition. However, in the case of the CuCl molecule this  $A'$  band appears quite low in energy. As was already pointed out by Hikmet *et al.*<sup>19</sup> if one considers the energy diagram of the electronic states of CuF, CuCl, and CuBr,<sup>20</sup> the energy of a given state increases with the atomic number of the halogen. That holds for all the states but for the  $A'$  transition of CuCl.<sup>18</sup> Moreover, some other studies assign the  $^3\Sigma_1^+ \rightarrow X^1\Sigma^+$  transition to the  $A$  band appearing at  $19\,035\text{ cm}^{-1}$ .<sup>21,22</sup> The characterization and assignment of the  $A'$  band in CuCl seems unclear and is still an open question since several attempts to find it via laser spectroscopy have failed.<sup>21</sup> Recently, Delaval *et al.*<sup>21,23</sup> made a study of the radiative lifetimes in CuCl and made a comparison with the well established results in the CuF molecule. These authors found the  $B$  and  $C$  states to correspond to the  $^3\Pi_1$  and  $^3\Pi_0$  components of the  $3d$ -hole  $^3\Pi$  state, the  $D$  and  $E$  states are the  $^1\Pi$  and the  $^1\Sigma^+$   $3d$ -hole states, respectively, and the  $F$  system corresponds to the  $^3\Delta_1$  component. The  $A$  system was first assigned to the  $^3\Pi_2$  component of the  $3d$ -hole  $^3\Pi$  state,<sup>23</sup> and later reassigned to the  $\Omega = 1$  component of  $^3\Sigma^+$ .<sup>21</sup>

The only dipole allowed transitions within the Born-Oppenheimer approximation correspond to  $^1\Sigma^+ \rightarrow X^1\Sigma^+$  and  $^1\Pi \rightarrow X^1\Sigma^+$ , thus the triplet-singlet transitions, which are allowed due to spin-orbit coupling, show generally smaller intensities than the allowed singlet-singlet ones.<sup>23</sup> From the experimental data it seems that the position of the bands is well defined, but the discussion above illustrates that the assignment of these bands to the different excitations is still not well defined.

Several theoretical studies have been done. Nguyen *et al.*<sup>3</sup> estimated the adiabatic excitation energies, equilibrium bond distances, and harmonic vibrational frequencies for some diatomic copper species at the SCF level and by

second- to fourth-order Møller–Plesset perturbation theory. For CuCl they found, at the fourth-order of perturbation, the following ordering for the excited states:  $^3\Sigma^+$ ,  $^3\Pi$ ,  $^1\Pi$ ,  $^3\Delta$ , and  $^1\Delta$ . Winter and Huestis<sup>22</sup> studied the low-lying excited states within the Hartree–Fock approximation and including spin–orbit interaction semiempirically using an atoms-in-molecules technique. These authors propose the following assignment: the  $^3\Sigma_1^+$ ,  $^3\Pi_1$ ,  $^3\Pi_0$ ,  $^3\Delta_1$ ,  $^1\Sigma_0^+$ , and  $^1\Pi_1$  correspond to the A, B, C, D, E, and F structures, respectively. Recently, Ramírez-Solís *et al.*<sup>24–26</sup> performed a series of MCSCF followed by MRCI calculations to estimate the electronic transition energies and transition dipole moments of the six lowest excited states. Scalar relativistic effects were included through relativistic effective core potentials. These authors found the following ordering  $X\ ^1\Sigma^+$ ,  $^3\Sigma^+$ ,  $^3\Pi$ ,  $^1\Sigma^+$ ,  $^3\Delta$ ,  $^1\Pi$ , and  $^1\Delta$ .

In the course of work on the spectrum of solid CuCl we have also studied the excitation spectrum of diatomic CuCl in order to determine the character of the lower lying transitions. The results obtained for the ionization and excitation spectra of solid CuCl will be published in the near future. For this study we use the recently developed CASSCF/CASPT2 approach.<sup>27,28</sup> In the CASSCF wave function the most important electron correlation contributions due to near degeneracies are taken into account. Most of the remaining part of the electron correlation is treated in the following CASPT2 step by second order perturbation theory, with the CASSCF wave function as zeroth-order wave function. This approach has become a powerful method to accurately study excited states. It has been successfully applied to the study of several organic molecules,<sup>29,30</sup> some transition metal compounds, as diatomic molecules<sup>31</sup> or transition metal complexes,<sup>32,33</sup> and recently to the study of local  $d$ – $d$  excitations in solid NiO.<sup>34</sup>

Finally, it is important to get an impression of the effect of spin–orbit coupling on the character and the relative position of the excited states. This is in particular interesting because of the suggestion of Burghardt *et al.*<sup>17</sup> that the D and E states are mixtures of  $^1\Pi_1$  and  $^3\Delta_1$ . Therefore four-component relativistic valence CI (VCI) results are compared with nonrelativistic VCI results.

## II. COMPUTATIONAL DETAILS

The major part of the calculations was performed using the CASSCF/CASPT2 approach<sup>27,28</sup> which is implemented in the MOLCAS-3 quantum chemistry software.<sup>35</sup>

The basis sets used in the CASSCF/CASPT2 calculations are derived from the (21s15p10d6f) primitive basis set for Cu and (17s12p5d) for Cl. An ANO general contraction scheme was used resulting in final [7s6p3d1f] and [5s4p1d] basis sets for Cu and for Cl, respectively.<sup>36,37</sup> In some of the calculations, namely those in which 3s and 3p correlation effects are taken into account, the basis set on Cu was enlarged by uncontracting four s, p, and d functions in the appropriate region, leading to the final [11s10p7d1f] basis set. A first order treatment of the scalar relativistic

effects,<sup>38</sup> the mass–velocity and Darwin terms, was included in the calculations.

For the CuCl diatomic molecule  $C_{2v}$  symmetry was imposed. For comparative purposes, the lowest states of free Cu and Cu<sup>+</sup> have also been analyzed. These calculations were performed in  $D_{2h}$  symmetry. However, extra symmetry restrictions were imposed in order to recover the actual spherical symmetry by preventing the mixing between orbitals that belong to different symmetry representations in the spherical symmetry.

In order to study the different contributions to the excitation energies in the Cu<sup>+</sup> ion, three sets of CASSCF/CASPT2 calculations were performed. First, only the 3d and 4s orbitals were chosen as active orbitals. In the second set of calculations a second Cu 3d shell (3d') was incorporated in the CASSCF step. Finally, the possible effects due to the 4s–4p near degeneracy were studied by including the 4p orbitals in the active space. Using these CASSCF wave functions as a reference, CASPT2 calculations were performed to estimate the remaining correlation effects. First, the effect of the valence correlation energy was studied by correlating only the 3d and 4s valence electrons; these calculations are denoted as CASPT2(v). The contribution to the second order energy due to the correlation of the core–core and core–valence electron pairs was analyzed by including also the 3s and 3p electrons of Cu. In these calculations, denoted as CASPT2(c–v), the larger basis set on Cu was used.

Analogously, to study the transition energies in the CuCl molecule we have performed CASSCF calculations including the 3d, 3d', and 4s orbitals in the active space. Only for some states a larger active space including also one 3p orbital on Cl was needed. Again, the different contributions to the second order correlation energy were determined by correlating first, the valence electrons, i.e., Cu(3d,4s) and Cl(3s,3p), and second, also the core Cu(3s,3p) electrons.

The effects of relativity, in particular spin–orbit interactions, were further analyzed by comparing four-component relativistic and nonrelativistic valence shell CI (VCI) results. These calculations were done with the MOLDIR program package<sup>39</sup> developed in our laboratory for relativistic Fock–Dirac-CI and coupled cluster<sup>40,41</sup> calculations. The basis set for Cl used for these calculations is the same as described in Ref. 42. For Cu we used a large component primitive basis set (21s16p10d3f), of which the exponents were relativistically optimized using the GRASP program,<sup>43,44</sup> whereas the small component basis set (16s31p16d10f3g) was generated using the kinetic balance relation. These primitive sets were contracted to [7s9p6d3f] and [7s12p9d6f3g], respectively.<sup>45</sup> The point group symmetry imposed in the VCI calculations is the  $C_{4v}^*$  double group. A Gaussian distribution is used to represent the spatial extent of the nuclei in both the relativistic and nonrelativistic VCI calculations. The VCI contained all configurations based on Cu<sup>+</sup>(3d<sup>9</sup>4s<sup>1</sup>)Cl<sup>–</sup>(3p<sup>6</sup>). The basis of spinors was optimized for the weighted average of all states derived from the basic configuration Cu<sup>2+</sup>(3d<sup>9</sup>)Cl<sup>–</sup>(3p<sup>6</sup>) of the CuCl<sup>+</sup> ionized system. Optimization of the spinors, including the Cu(4s), by minimizing a weighted average of all state energies arising

TABLE I. Atomic transition energies (in eV) for  $\text{Cu}^+$ . The CASSCF active space includes six orbitals,  $\text{Cu}(3d) + \text{Cu}(4s)$ . In parentheses are the energies with respect to the  $\text{Cu}(^2S)$  ground state.

State	CASSCF <sup>a</sup>	CASSCF	CASPT2( $v$ )	Weight	CASPT2( $c-v$ )	Weight	Experiment <sup>b</sup>
Cu $^2S(d^{10}s^1)$	0.00	0.00	0.00	0.920	0.00	0.896	0.00
$\text{Cu}^+$ $^1S(d^{10})$	0.0 (6.38)	0.0 (6.54)	0.0 (7.47)	0.932	0.0 (7.54)	0.909	0.0 (7.72)
$^3D(d^9s^1)$	1.37	0.90	3.45	0.951	3.71	0.927	2.82
$^1D(d^9s^1)$	1.77	1.33	3.85	0.950	4.14	0.926	3.25

<sup>a</sup>Scalar relativistic effects are not included.<sup>b</sup>Reference 48.

from the configuration  $\text{Cu}^+(3d^9 4s^1)\text{Cl}^-(3p^6)$  of neutral CuCl might be preferable, but the capability of having two open shells in the same symmetry is presently not implemented in the SCF part of MOLFDIR. However, it is not to be expected that occupying the  $\text{Cu}(4s)$  like spinor of  $a_1$  symmetry in the optimization step will change the splitting of the  $3d$  hole states of CuCl drastically. A possible effect of occupying the  $\text{Cu}(4s)$  spinor could be a stabilization of the  $\Sigma^+$  states.

### III. RESULTS AND DISCUSSION

#### A. Free Cu and $\text{Cu}^+$

The first excited states of CuCl are expected to be related to excitations from  $\text{Cu}^+(3d^{10})$ ,  $\text{Cl}^-(3s^2 3p^6)$  to  $\text{Cu}^+(3d^9 4s^1)$ ,  $\text{Cl}^-(3s^2 3p^6)$ . Therefore we have first studied the lowest states of  $\text{Cu}^+$ . For comparison results for the ground state of Cu are also shown. The relevant excitations correspond to transitions from the  $\text{Cu}^+$  ground state,  $^1S(d^{10})$ , to the  $^3D$  and  $^1D$  excited states arising from the  $3d^9 4s^1$  atomic configuration.

First, we have constructed the CASSCF reference wave functions considering an active space formed by the  $3d$  and  $4s$  orbitals, containing 11 electrons for Cu and 10 for  $\text{Cu}^+$ . While for the  $^1S(d^{10})\text{Cu}^+$  state some correlation is already introduced at this level through the active  $4s$  orbital, for the rest of states these calculations correspond to an open shell Hartree–Fock calculation. The CASSCF, CASPT2( $v$ ), and CASPT2( $c-v$ ) results obtained with this active space are presented in Table I. The weights of the reference in the first order correction to the wave function,  $\omega$ , and the experimental energies are also given in the table.

It is well known that electron correlation effects are of substantial importance in the calculation of excitation energies of transition metal atoms and their compounds. Moreover, relativistic effects, which tend to stabilize the

$s$ -electron rich configurations, contribute significantly. This can be seen in Table I, where the CASSCF excitation energies without considering these effects are also reported. The contribution of the scalar relativistic effects to the excitation energies is of the order of 0.45 eV, i.e., of the same order as found by Martin and Hay<sup>46</sup> who performed numerical Hartree–Fock calculations including relativistic core corrections. Therefore, in all CASSCF/CASPT2 results on CuCl reported in this work a first order correction of the scalar relativistic effects has been taken into account.

The results in Table I show that the CASSCF excitation energies are in error by about 1–1.5 eV with respect to the experimental values whereas the CASPT2( $v$ ) and CASPT2( $c-v$ ) values differ by about 1 eV. Only the  $^3D-^1D$  splitting almost agrees with experiment at both levels of calculation, showing, as expected, that the electron correlation effects are similar for singlet and triplet coupling. From the table it can also be seen that the weight of the CASSCF reference wave function in the total first-order wave function slightly decreases when the number of electrons in the  $3d$  shell increases, i.e., when the effect of the  $3d$  correlation becomes more important. Both results, the discrepancy in the excitation energies and the variation in the weights, indicate that some essential effect has still not been considered. As has been previously noticed,<sup>47</sup> the  $3d$  electron correlation effects are not sufficiently accounted for by CASPT2 and to obtain a more balanced description a second  $3d$  shell ( $3d'$ ) should be included in the active space at the CASSCF level.

Next we have extended the active space to 11 orbitals by including a new set of five orbitals which after optimization indeed turned out to be  $3d'$ -type orbitals. The results of the CASSCF and CASPT2 calculations are listed in Table II. The CASSCF excitations energies reported differ by about 0.3 eV from the experimental values. This discrepancy is reduced in the CASPT2 results; 0.09 eV at the

TABLE II. Atomic transition energies (in eV) for  $\text{Cu}^+$ . The CASSCF active space includes 11 orbitals,  $\text{Cu}(3d) + \text{Cu}(3d') + \text{Cu}(4s)$ . In parentheses are the energies with respect to the  $\text{Cu}(^2S)$  ground state.

State	CASSCF	CASPT2( $v$ )	Weight	CASPT2( $c-v$ )	Weight	Experiment <sup>a</sup>
Cu $^2S(d^{10}s^1)$	0.00	0.00	0.972	0.00	0.949	0.00
$\text{Cu}^+$ $^1S(d^{10})$	0.0 (6.66)	0.0 (7.36)	0.982	0.0 (7.39)	0.960	0.0 (7.72)
$^3D(d^9s^1)$	2.55	2.78	0.981	2.68	0.958	2.82
$^1D(d^9s^1)$	2.98	3.16	0.979	3.09	0.957	3.25

<sup>a</sup>Reference 48.

TABLE III. Atomic transition energies (in eV) for  $\text{Cu}^+$ . The CASSCF active space includes 14 orbitals,  $\text{Cu}(3d) + \text{Cu}(3d') + \text{Cu}(4s) + \text{Cu}(4p)$ . In parentheses are the energies with respect to the  $\text{Cu}(^2S)$  ground state.

State		CASSCF	CASPT2( $v$ )	Weight	CASPT2( $c-v$ )	Weight	Experiment <sup>a</sup>
Cu	$^2S(d^{10}s^1)$	0.00	0.00	0.976	0.00	0.954	0.00
$\text{Cu}^+$	$^1S(d^{10})$	0.0 (6.80)	0.0 (7.45)	0.985	0.0 (7.36)	0.961	0.0 (7.72)
	$^3D(d^9s^1)$	2.58	2.78	0.983	2.78	0.960	2.82
	$^1D(d^9s^1)$	2.98	3.17	0.983	3.20	0.960	3.25

<sup>a</sup>Reference 48.

CASPT2( $v$ ) level and 0.15 eV after inclusion of the core–valence correlation, CASPT2( $c-v$ ).

The largest active space considered is formed by the  $3d$ ,  $3d'$ ,  $4s$ , and  $4p$  orbitals, that is, 14 orbitals and 11 and 10 electrons for Cu and  $\text{Cu}^+$ , respectively. The results obtained with this active space are collected in Table III. The CASSCF and CASPT2( $v$ ) transition energies of the  $\text{Cu}^+$  cation are almost the same as the values reported in Table II since the  $4p$  orbitals do not play an important role for these states. The values obtained in the CASPT2( $c-v$ ) calculations are close to the CASPT2( $v$ ) ones and differ about 0.05 eV from the experimental data. However, comparing the CASPT2( $c-v$ ) values from Tables II and III there is a difference of about 0.1 eV. A closer look at the different contributions to the second order energy shows that in both cases the effect of the correlation due to the core–core and core–valence electron pairs is very small but they contribute with opposite sign in the computed excitation energies leading to such a difference. Finally, one can see from Tables I–III that all calculations yield about the same ionization energy for Cu since both states have the same  $d$  occupancy. Its value is about 0.3 eV less than that found experimentally.

From the results discussed above we conclude that the transition energies in  $\text{Cu}^+$  are properly described when the  $3d$ ,  $3d'$ , and  $4s$  orbitals are included in the CASSCF step. The inclusion of the second  $3d$  shell is essential to reach an accurate description, providing the flexibility needed to account for the different  $d$  occupancies. This has been previously noticed in the study of other transition metal compounds.<sup>32,34</sup> The inclusion of the correlation due to the  $3s$  and  $3p$  core electrons has only a small effect on the excitation energies.

The accurate description obtained for the  $\text{Cu}^+$  atomic spectra shows the efficiency and quality of the theoretical approach used in this work and encourages us to study the more complicated CuCl spectra with this approach.

## B. Excitation spectra of CuCl

As commented above, the lower excited states of the CuCl molecule can all be related to the formal ionic configuration  $\text{Cu}^+(3d^94s^1)\text{Cl}^-(3s^23p^6)$ . Considering the results obtained for the  $\text{Cu}^+$  cation it is reasonable to include the  $3d$ ,  $3d'$ , and  $4s$  orbitals in the CASSCF step in order to obtain a good description of the excitation spectrum in the molecule. Therefore, we performed CASSCF calculations for the ground and the six lowest excited states considering these 11 orbitals and 10 active electrons. Taking these wave

functions as a reference we performed again two sets of CASPT2 calculations, one where only the valence electrons were correlated, i.e.,  $3d, 4s$  in copper and  $3s, 3p$  in chlorine, and a second one where the  $3s, 3p$  core electrons in copper were also included.

The main configurations appearing in the CASSCF wave functions for the various states are

$$X\ ^1\Sigma^+ : [\text{core}](9\sigma)^2(4\pi)^4(1\delta)^4(10\sigma)^2(11\sigma)^2(5\pi)^4,$$

$$^3\Pi, ^1\Pi : [\text{core}]$$

$$\times (9\sigma)^2(4\pi)^3(1\delta)^4(10\sigma)^2(11\sigma)^2(5\pi)^4(12\sigma)^1,$$

$$^3\Delta, ^1\Delta : [\text{core}]$$

$$\times (9\sigma)^2(4\pi)^4(1\delta)^3(10\sigma)^2(11\sigma)^2(5\pi)^4(12\sigma)^1,$$

$$^1\Sigma^+, ^3\Sigma^+ : [\text{core}]$$

$$\times (9\sigma)^2(4\pi)^4(1\delta)^4(10\sigma)^1(11\sigma)^2(5\pi)^4(12\sigma)^1.$$

These orbitals appear to be rather localized. Thus, the  $9\sigma$  is mainly the  $\text{Cl}(3s)$  orbital, the  $4\pi$ ,  $1\delta$ , and  $10\sigma$  are the  $3d$  orbitals of Cu, the  $11\sigma$  and  $5\pi$  the  $\text{Cl}(3p)$  orbitals, and the  $12\sigma$  is mainly built up by the Cu  $4s$  orbital with a small contribution on chlorine  $3p$ . Therefore, the results indeed present an ionic description of CuCl, where the ground state is well represented by the  $\text{Cu}^+(3d^{10})\text{Cl}^-(3s^23p^6)$  configuration and the excited states by the  $\text{Cu}^+(3d^94s^1)\text{Cl}^-(3s^23p^6)$  configuration. However, for the states of  $\Sigma^+$  symmetry the CASSCF active space formed by 11 orbitals was not enough to give an accurate description. The weight of the CASSCF reference wave function in the first order wave function was low and it changed drastically when the Cu–Cl distance was varied. On inspection the  $\text{Cl}(3p\sigma)$  orbital turned out to give an important contribution to the first order wave function, especially close to the equilibrium geometry. Therefore for the  $^3\Sigma^+$  and  $^1\Sigma^+$  states the latter orbital was added to the CASSCF active space leading to 12 orbitals and 12 electrons. With this larger active space the CASSCF energy for both states was lowered by around 0.12 eV and a good description of the CASPT2 potential curve was obtained. Two configurations predominate in the CASSCF wave function for the  $^3\Sigma^+$  state; the ionic configuration  $([\text{core}](9\sigma)^2(4\pi)^4(1\delta)^4(10\sigma)^1(11\sigma)^2(5\pi)^4(12\sigma)^1)$  is the most important one, with a weight of about 93%, followed by a charge transfer configuration with the hole located in the  $\text{Cl}(3p\sigma)$  orbital,  $([\text{core}](9\sigma)^2(4\pi)^4(1\delta)^4(10\sigma)^2(11\sigma)^1(5\pi)^4(12\sigma)^1)$ , and a weight of 4%. This state hence has more covalent charac-

TABLE IV. Spectroscopic constants for the low-lying electronic states calculated at the CASPT2( $c-v$ ) level for  $^{65}\text{CuCl}$ . Available experimental data in parentheses.<sup>a</sup>

State	$R_e$ (a.u.)	$\omega_e$ ( $\text{cm}^{-1}$ )	$B_e$ ( $\text{cm}^{-1}$ )	$\alpha_e$ ( $10^{-3} \text{ cm}^{-1}$ )	$D_e$ ( $10^{-7} \text{ cm}^{-1}$ )
$X^1\Sigma^+$	3.891 (3.878)	414 (415)	0.175 (0.176)	1.10 (1.00)	1.26 (1.27)
$^3\Sigma^+$	4.001	387	0.165	2.12	1.27
$^3\Pi$	4.007 (3.968) <sup>b</sup>	394 (399) <sup>b</sup>	0.165 (0.169) <sup>b</sup>	1.07 (0.92) <sup>b</sup>	1.15 (1.2) <sup>b</sup>
$^1\Pi$	4.015 (3.974)	399 (393)	0.164 (0.167)	0.91 (0.98)	1.12 (1.2)
$^1\Sigma^+$	4.016 (3.990)	417 (403)	0.164 (0.166)	1.00 (1.08)	1.02 (1.0)
$^3\Delta$	4.067 (4.060)	386 (385)	0.160 (0.160)	0.96 (0.91)	1.11 (1.2)
$^1\Delta$	4.058	391	0.161	0.96	1.10

<sup>a</sup>Reference 20.<sup>b</sup>For the  $^3\Pi_1$  spin-orbit component.

ter. For the  $^1\Sigma^+$  state the wave function shows a contribution of 14% of the closed-shell configuration ( $[\text{core}](9\sigma)^2(4\pi)^4(1\delta)^4(10\sigma)^2(11\sigma)^2(5\pi)^4$ ), whereas the main configuration has a weight of 73%, a charge transfer configuration where the hole is in  $\text{Cl}(3p\sigma)$  contributes with 5% and a configuration ( $[\text{core}](9\sigma)^2(4\pi)^4(1\delta)^4(10\sigma)^0(11\sigma)^2(5\pi)^4(12\sigma)^2$ ) has a weight of 4%. The possible mixing of this wave function with the ground state wave function will be discussed further below.

The importance of the second Cu  $3d$  shell in the active space is worth noting. These orbitals act as correlating orbitals for the  $3d$  electrons and have different effects for the different  $d^n$  configurations. For the  $3d^{10}$  ground state the  $d'$  occupation numbers are around 0.017 and for the excited states the occupations are slightly smaller, about 0.010.

Based on the CASSCF wave functions discussed above, we have performed CASPT2 calculations correlating the valence and core electrons in a range of internuclear distances for all the states. In Table IV the spectroscopic constants for  $^{65}\text{CuCl}$  obtained at the CASPT2 ( $c-v$ ) level for the ground and excited states are listed. The calculated equilibrium distances are between 0.01 and 0.04 a.u. larger than the ones derived from the spectroscopic data, which is slightly closer than obtained in MRCI calculations.<sup>24</sup> The agreement for the remaining molecular constants is also satisfactory.

In Table V we present the CASSCF, CASPT2( $v$ ), and CASPT2( $c-v$ ) vertical de-excitation energies, calculated at the equilibrium distances of each excited state [i.e., the CASPT2( $c-v$ ) values as shown in Table IV], together with the experimental values obtained by Delaval *et al.* from fluorescence decay experiments.<sup>21,23</sup> The results obtained for the adiabatic transitions are not reported but they are quite close to the vertical ones. This is because the equilibrium distances for all states are essentially the same. In fact, all the states share a nearly common set of vibrational and rotational spectroscopic constants<sup>20</sup> and therefore the zero point energy correction is negligible. From the results in Table V, first notice that the CASSCF excitation energies give the same ordering of the states as the CASPT2 results. The latter values are all shifted up by 0.2–0.3 eV. Actually, the singlet–triplet splittings of each symmetry are almost the same at both levels of approximation, namely about 0.28 eV for the  $\Delta$  states, 0.33 eV for the  $\Pi$  states, and around 0.48 eV for the  $\Sigma^+$  excited states, showing again that the correlation effects are quite

similar for the triplet and singlet states. As has been previously noticed for  $\text{Cu}^+$ , the contribution of the correlation of the Cu  $3s$  and  $3p$  electrons to the excitation energies is fairly small, about  $300 \text{ cm}^{-1}$ .

In Table V our results corresponding to pure electronic states are compared with the experimental values assigned by Delaval *et al.* For the first excited state, namely the  $^3\Sigma^+$  state, the error is around  $1300 \text{ cm}^{-1}$ . We have to point out, however, that the excitation energies for this  $^3\Sigma^+$  state, for which 12 active orbitals were included in the CAS space, have been calculated with respect to the ground state described with 11 active orbitals. This can give an unbalanced description of this excitation because of the slightly different quality of the calculations. In fact, the inclusion of the  $\text{Cl}(3p\sigma)$  orbital in the active space of the excited state calculations leads to an extra stabilization of about 0.1 eV of the CASSCF energy, thus leading to a decrease in the excitation energy. On the other hand, adding an extra orbital in the CAS space for the ground state leads to a result that is not directly comparable to the  $^3\Sigma^+$  excited state result. This is because charge transfer cannot occur in the ground state and the extra orbital becomes a Cu( $3p$ ) instead of a Cl( $3p\sigma$ ), leading to a different treatment of the electron correlation effects in both states. For the ground state, part of the core correlation is hence treated variationally whereas for the  $^3\Sigma^+$  this is done by perturbation theory only. Realizing that CASPT2 tends to overestimate the correlation energy, one has to be cautious in comparing the results when the character of active orbitals differs from state to state. In the present

TABLE V. Vertical transition energies in  $\text{cm}^{-1}$  (from the minimum of each excited state downwards). Experimental values correspond to the assignment suggested by Delaval *et al.*<sup>a</sup>

State	CASSCF	CASPT2( $v$ )	CASPT2( $c-v$ )	Experiment
$X^1\Sigma^+$	0	0	0	0
$^3\Sigma^+$	15 573	17 726	17 659	19 035
$^3\Pi$	17 929	20 180	20 203	20 486
				20 648
$^1\Pi$	20 797	22 793	22 894	22 987
$^1\Sigma^+$	19 767	21 467	21 492	23 067
$^3\Delta$	19 733	22 143	22 209	25 326
$^1\Delta$	22 030	24 240	24 442	

<sup>a</sup>References 21 and 23.

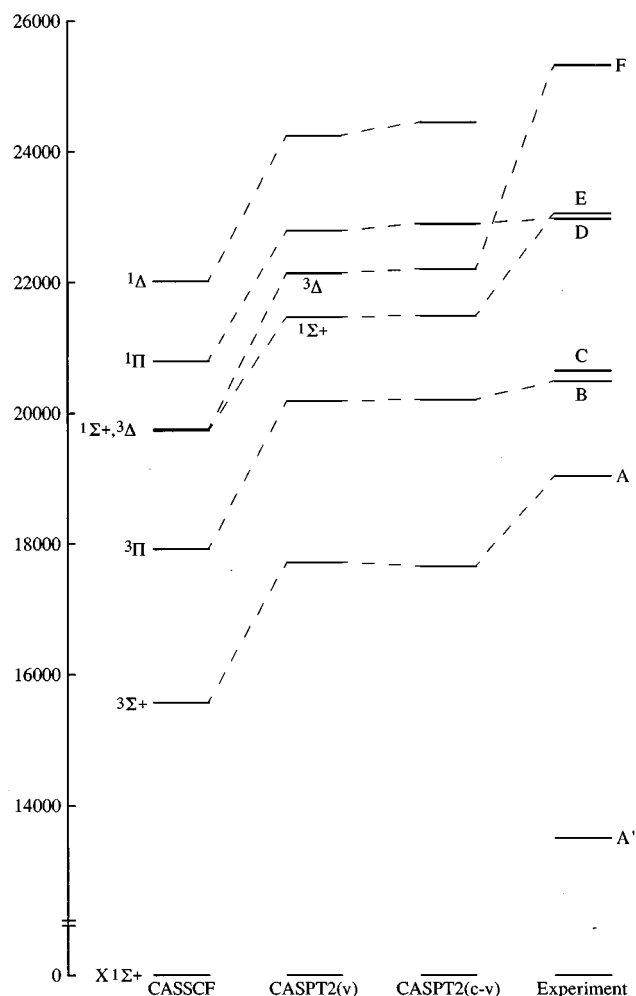


FIG. 1. Level diagram of the electronic transitions in diatomic CuCl. The vertical transition energies (in  $\text{cm}^{-1}$ ) at the CASSCF, CASPT2( $v$ ), and CASPT2( $c-v$ ) levels (results from Table V) and the experimental data corresponding to the assignment suggested by Delaval *et al.* (Refs. 21, 23) are presented.

case, we observe that CASPT2 grossly overestimates the  $\text{Cu}(3p)$  correlation. Therefore, it is better to treat the core correlation in the perturbational step for all the states because the overestimation is about the same for all of them and does not influence the excitation energies. The same holds for the  $1\Sigma^+$  state, which appears  $1500\text{ cm}^{-1}$  lower than the observed transition. Concerning the  $3\Pi$  and  $1\Pi$  states there is excellent agreement between calculated and experimental transition energies. However for the  $3\Delta$  state the error is larger, about  $3000\text{ cm}^{-1}$ .

A level diagram of the different states is shown in Fig. 1. Comparison of the CASPT2( $c-v$ ) results with the MRCI results obtained by Ramírez-Solís *et al.*<sup>24</sup> shows that the values of the transition energies obtained with both methods are quite close. These authors gave the following values for the vertical transitions:  $3\Sigma^+$ : 16 234,  $3\Pi$ : 19 627,  $1\Pi$ : 22 980,  $1\Sigma^+$ : 20 558,  $3\Delta$ : 22 412, and  $1\Delta$ : 23 688  $\text{cm}^{-1}$ . The authors pointed out the difficulty of describing properly the  $1\Sigma^+$  state, which has the same symmetry and spin multiplicity as

the  $X\ 1\Sigma^+$  ground state, thus allowing a mixing between them. As was discussed above, this problem can appear also in our description of the two states. Therefore, we further analyzed the CASSCF results for these states, with 11 orbitals in the active space, using orbitals optimized separately for both  $X\ 1\Sigma^+$  and  $1\Sigma^+$  states. The CASSCF excitation energy is 2.57 eV. The two CASSCF wave functions are mutually nonorthogonal; their overlap is 0.099. We performed a  $2\times 2$  CI (or “state interaction”) between the two separately optimized CASSCF wave functions to remove the interaction between them. This gives an excitation energy of 2.59 eV for the  $1\Sigma^+$  state, thus only 0.02 eV larger than when the overlap and interaction are neglected. The small increase shows that the mixing of the ground state wave function into the  $1\Sigma^+$  excited state wave function does not lead to a severe underestimation of the excitation energy of this state.

Table VI shows a comparison between four-component relativistic VCI and nonrelativistic VCI results for the excited states. The distance used in these calculations is the experimental ground state distance, 3.878 bohr. The basis of spinors was optimized for the weighted average of all states derived from the configuration  $\text{Cu}^{2+}(3d^9)\text{Cl}^-(3p^6)$  of the  $\text{CuCl}^+$ . This spinor basis is not suited to describe the ground state, but it should present a reasonable description of the relative energies of  $\text{Cu}^+(3d^94s^1)\text{Cl}^-(3p^6)$  type excited states. Therefore, excitation energies respect to the lowest  $3\Sigma^+$  excited state are reported on Table VI. The CI expansion contains all configurations based on  $\text{Cu}^+(3d^94s^1)\text{Cl}^-(3p^6)$ . The mixing between the states, due to spin-orbit coupling, is also showing in the table. For comparison, nonrelativistic CASSCF energies were also computed at the same equilibrium geometry. In this case, only six orbitals were included in the active space [ $5\text{Cu}(3d)$  and  $\text{Cu}(4s)$ ] with 10 active electrons, so here  $\text{Cu}^+(3d^{10})$  and  $\text{Cu}^+(3d^84s^2)$  configurations are also included on the orbital optimization. For the  $1\Sigma^+$  state that was not possible and the figure shown in Table VI correspond to a CASSCF with 11 orbitals as has been previously described. Both the relativistic and nonrelativistic results obtained by Winter *et al.*,<sup>22</sup> based on Hartree-Fock (HF) calculations at the computed equilibrium distance (4.2 a.u.) and semiempirical inclusion of the spin-orbit coupling, are also summarized.

The nonrelativistic VCI relative energies are reasonably close to the CASSCF and the SCF values obtained by Winter *et al.*<sup>22</sup> Concerning the relativistic results, first one can notice that the relative energies obtained by VCI calculations are quite close to those obtained by Winter *et al.*,<sup>22</sup> specially for the triplet states. The spin-orbit splitting turned out to be about  $97\text{ cm}^{-1}$  for the  $3\Sigma$  states,  $1567\text{ cm}^{-1}$  for the  $3\Pi$ , and  $1503\text{ cm}^{-1}$  for the  $3\Delta$  states. Comparing both the relativistic and nonrelativistic VCI relative energies for the singlet states one sees that the spin-orbit coupling shifts up the former by about  $700\text{--}1200\text{ cm}^{-1}$ . That shows that the ordering and the relative positions of the excited states are not affected by the inclusion of the relativistic effects. The relative energies showed in Table VI are within  $1000\text{ cm}^{-1}$  comparing to the equivalent experimental energy differences of Delaval *et al.*

TABLE VI. Relative energies (in  $\text{cm}^{-1}$ ) of the lowest excited states of CuCl at the equilibrium distance of the ground state. Valence CI expansions include all CSF's derived from  $\text{Cu}^+(3d^9 4s^1) \text{Cl}^-(3p^6)$ . In the CASSCF calculations six active orbitals [5 Cu(3d) and Cu(4s)] and 10 electrons were included. The relativistic mixing of the VCI wave functions is also shown.

State	Nonrelativistic			Relativistic		
	VCI	CASSCF	SCF <sup>a</sup>	VCI	VCI mixing	SCF <sup>a</sup>
$^3\Sigma_{0-}$	0	0	0	0	6% $^3\Pi_{0-}$	80
$^3\Sigma_1$				97	9% $^3\Pi_1$	0
$^3\Pi_2$				943	1% $^3\Delta_2$	1290
$^3\Pi_1$				1574	9% $^3\Sigma_1$	1774
$^3\Pi_{0+}$	1187	1755	1580	1615	29% $^1\Sigma_{0+}$	2016
$^3\Pi_{0-}$				2510	6% $^3\Sigma_{0-}$	2500
$^3\Delta_3$				2579		2291
$^3\Delta_2$				3180	1% $^3\Pi_2$	3017
$^3\Delta_1$	3098	3907	3095	4082	48% $^1\Pi_1$	3968
$^1\Sigma_{0+}$	3623	3871 <sup>b</sup>	3270	4820	29% $^3\Pi_{0+}$	4073
$^1\Pi_1$	3897	4406	4170	5031	47% $^3\Delta_1$	6284
$^1\Delta_2$	5013	5959	5443	5877		7615

<sup>a</sup>Reference 22.

<sup>b</sup>CASSCF with 11 active orbitals.

for all states but for the  $^3\Delta_1$  state, for which the relative energy appears about  $2200 \text{ cm}^{-1}$  too low. The relativistic results also show the mixing between the different states, due to spin-orbit coupling. Particularly interesting is the almost one to one mixing between the  $^1\Pi_1$  and the  $^3\Delta_1$  states, in agreement with the suggestion of Burghardt *et al.*<sup>17</sup> based on laser excitation spectroscopy. A more detailed relativistic study including the most important correlation effects will be published separately.

On the basis of our results a reasonable description of the CuCl spectra was reached. The  $^3\Pi$  and  $^1\Pi$  states are well described; thus the two bands appearing around  $20\,000 \text{ cm}^{-1}$ , the *B* and *C* bands, are assigned to different spin-orbit components of the  $^3\Pi$  state, as suggested by Delaval *et al.*<sup>21,23</sup> and Winter *et al.*<sup>22</sup> The  $^3\Sigma^+ \rightarrow X^1\Sigma^+$  transition appears around  $17\,700 \text{ cm}^{-1}$  and it is more likely to correspond to the *A* band observed around  $19\,000 \text{ cm}^{-1}$  than to the *A* around  $13\,500 \text{ cm}^{-1}$  proposed by Balfour *et al.*<sup>18</sup> The influence of the relativistic effects in this band is shown to be rather small. Thus, we believe that the  $^3\Sigma^+ \rightarrow X^1\Sigma^+$  transition corresponds to the experimentally reported *A* band since there is not any physical mechanism which could explain the much lower *A* excitation. The description obtained for the  $^1\Sigma^+$  state is also satisfactory. The only exception is the  $^3\Delta$  state (*F* band). The calculated excitation energy is about  $3000 \text{ cm}^{-1}$  below the *F* band, which is commonly assigned to a transition from the  $^3\Delta$  multiplet. However, this discrepancy seems to appear in all computational results published so far.

#### IV. CONCLUSIONS

The lower parts of the spectra of  $\text{Cu}^+$  and the diatomic molecule CuCl have been studied theoretically using the recently developed CASSCF/CASPT2 approach. Various CASSCF wave functions including different active spaces have been studied. It has been shown that to reach an accu-

rate description of the excitation energies the inclusion of a second 3d shell into the reference space is essential. The atomic spectrum of  $\text{Cu}^+$  is reproduced within 0.05 eV of the experimental data. The electronic transition energies and spectroscopic constants of the six lowest excited states of the diatomic molecule CuCl have been studied. Results obtained with the CASPT2 method show good agreement with the experimental data. The present CASSCF/CASPT2 results compare well with previous MRCI results<sup>24</sup> showing that the CASSCF/CASPT2 approach offers a reliable alternative.

The relative positions of the excited states is not much influenced by inclusion of the relativistic effects. On the other hand, an estimate of the effect of spin-orbit interactions suggests a strong mixing between the  $^1\Pi_1$  and  $^3\Delta_1$  states, in agreement with the conclusions of Burghardt *et al.*<sup>17</sup> Based on our results the  $^3\Sigma^+ \rightarrow X^1\Sigma^+$  transition is assigned to the observed *A* band.

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